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PP-A52 NUCLEOPHILIC RING OPENING OF AZIRIDINES IN LIQUID SULFUR DIOXIDE

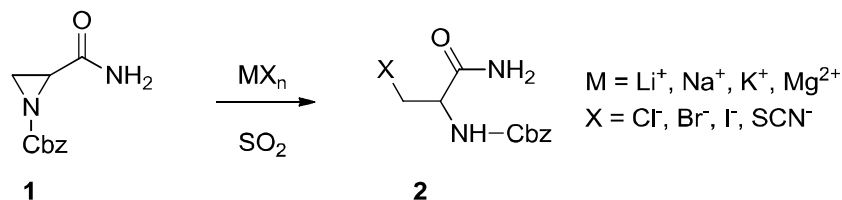
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Aziridine moiety represents one of the most frequently used three-membered ring systems in organic synthesis.¹ Because of the ring strain, opening of the aziridine cycle is the dominant reaction in their chemistry. The nucleophilic opening of aziridines has been exhaustively described in excellent reviews.² Halogen nucleophiles can be introduced under acid conditions (e.g.: with HCl).³ Another source of halogen nucleophiles are metal halides. Literature studies showed that there are only a few precedents of ring opening using halides MX_n . Righi and coworkers discovered that *N*-Boc-protected alkenylaziridine derivatives underwent regioselective ring opening with lithium halides when reaction was catalyzed by Amberlyst-15 in acetone (-20 °C).⁴ Substitution of Boc group to ethoxycarbonyl and the use of NaX instead of LiX led to reduced regioselectivity.⁵ An alternative combination of reagents is MgX_2/Et_2O .⁶ In the aforementioned examples the efficiency of the reaction depends strongly on substrate (activated/non-activated aziridine), nucleophile type and solvent.

Here we present a new synthetic process of aziridine **1** opening with metal halides and other nucleophiles in liquid sulfur dioxide. Reactions were carried out in three temperature modes: 1) low temp. (-70...-10 °C); 2) ambient temp. (20 °C) and 3) high temp. (60 °C).



The efficiency of each aziridine ring opening reaction was monitored in several solvents in parallel experiments: $\text{SO}_{2(\text{liq.})}$, DMSO, MeCN, TFE. We used I and II group metal halides as a nucleophile source. Results showed that the aziridine ring opening in liquid sulfur dioxide occurs noticeably faster and cleaner than in other solvents.

For example, NaCl required only 12 h at room temperature in liquid sulfur dioxide to form expected product **2a** ($X = \text{Cl}$) in almost quantitative yield.

In summary, we have discovered an effective synthetic approach for aziridine ring opening with metal halides in liquid sulfur dioxide. The results on the scope and limitations of this method using variously substituted aziridines and various nucleophiles will be discussed.

¹ Yudin, A. K. *Aziridines and epoxides in organic synthesis*, Wiley-VCH, Weinheim, 2006.

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³ Legters, J.; Thijs, L.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1992**, *11*, 16.

⁴ Righi, G.; Potini, C.; Bovicelli, P. *Tetrahedron Lett.* **2002**, *43*, 5867.

⁵ Righi, G.; D'Achille, R. *Tetrahedron Lett.* **1996**, *37*, 6893.

⁶ Righi, G.; Franchini, T.; Bonini, C. *Tetrahedron Lett.* **1998**, *39*, 2385.